Tailoring Properties of Epoxidized Natural Rubber via Transesterification Crosslinks

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Master of Science
in
Chemistry

by

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under the guidance of

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I, Shashank hereby declare that this dissertation titled **"Tailoring Properties of Epoxidized Natural Rubber via Transesterification Crosslinks"** is carried out by me in the **Department of Chemistry** of Visvesvaraya National Institute of Technology, Nagpur. The work is original and has not been submitted earlier whole or in part for the award of any degree/diploma at this or any other Institution / University.

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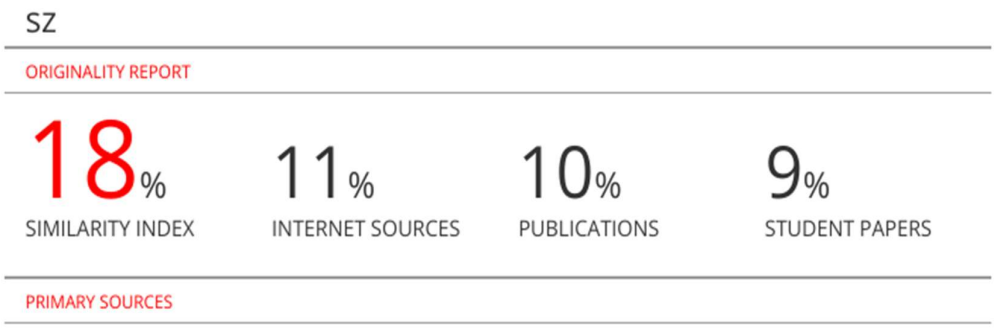

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Abstract

Elastomeric vitrimers represent a pioneering class of polymeric materials that bridge the gap between traditional thermosets and thermoplastics. They combine the dynamic crosslinking capabilities of thermosets with the mechanical robustness of elastomers, offering a new avenue for materials research and development. These materials exploit dynamic covalent bonds (DCBs) within a crosslinked network to achieve properties such as self-healing, recyclability and tunable mechanical performance.

In this study, we have employed Pripol-1017 in combination with a small quantity of metal ion in the form of $ZnCl_2$, to form dual cross-linking in epoxidized natural rbber (ENR-50). The use of Pripol-1017 results in the formation of beta-hydroxy ester linkage within the ENR-50 matrix via epoxide ring opening reaction between the carboxylic groups present in Pripol-1017 with the epoxide moiety of ENR-50. Zinc chloride acts as another cross-linker, to form a dynamic non-covalent network via interacting with hydroxyl group present in the ENR-50 matrix. Thorough investigation on the physicochemical properties of the synthesised materials has been done via Fourier transform infrared spectroscopy (FTIR), rheometric study, differential scanning calorimetry (DSC) and stress-strain study.

Keywords: transesterification, metal ligand crosslinking, stress-strain

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LIST OF SYMBOLS/ ABBREVIATION

Symbols/ Abbreviation	Full form
NR	Natural Rubber
ENR	Epoxidized Natural Rubber
1,2-DMI	1,2-Dimethyl Imidazole
FTIR	Fourier Transform Infrared Spectroscopy
DSC	Differential Scanning Calorimetry
UTM	Universal Testing Machine

CHAPTER 1
INTRODUCTION

1.1 Background:

Polymer materials have played a transformative role in material science over the decades, largely due to their exceptional versatility and compatibility with large-scale manufacturing processes like molding, extrusion, and hot pressing [1].Their inherent durability—marked by resistance to moisture, oxidation, and biological degradation—has further cemented their widespread use. Polymer are broadly classified into two categories: thermoplastics and thermosets. Thermoplastics, including materials such as polystyrene, polyethylene, PET (polyethylene terephthalate), and PVC (polyvinyl chloride), can be repeatedly melted and reshaped at elevated temperatures. In contrast, thermoset—such as epoxy, melamine, silicone, and urea-formaldehyde resins—undergo irreversible chemical crosslinking during curing, forming rigid three-dimensional molecular structures that offer superior mechanical strength and stability under heat and chemical exposure [2].

This fundamental structural difference explains their divergent recyclability. While thermoplastics consist of linear chains bonded by weak intermolecular forces, allowing them to soften upon heating, thermosets form permanent covalent bonds that create a single, insoluble, infusible network [3]. As a result, thermosets typically decompose before they can be re-melted, making traditional recycling methods ineffective. Most thermoset waste is therefore downcycled into filler materials or incinerated for energy recovery, rather than being returned to its original form [4].

Given these limitations, there is a growing interest in advanced engineering plastic materials that retain the desirable strength and durability of thermosets but can still be reprocessed at the end of their lifecycle. Developing such materials would be a crucial step toward establishing a circular economy, where products are not simply discarded but instead reused, repurposed, or converted into raw materials for new manufacturing cycles [5].

1.2 Vitrimer

Vitrimers are an emerging and fascinating class of materials that have garnered significant interest within the realm of polymer science. They fall under the broader category of dynamic covalent polymers and are characterized by their ability to undergo reversible bond exchange reactions when subjected to certain conditions. Unlike traditional thermosetting or thermoplastic polymers, vitrimers incorporate dynamic covalent bonds that can break and reform, enabling the material to be reshaped and repurposed without sacrificing its performance [6].

The molecular architecture of vitrimers typically involves dynamic bonds such as disulfide, imine, or boronic ester linkages. These allow the polymer network to reorganize itself, lending vitrimers their distinctive combination of thermoplastic malleability and thermoset robustness. This structural adaptability gives vitrimers a unique advantage over conventional polymers [7].

Due to their impressive physical and thermal characteristics, vitrimers are highly suitable for use in various demanding industries. They exhibit excellent mechanical strength, resilience, and flexibility, making them well-suited for extreme operational environments. Moreover, their superior heat resistance helps maintain structural integrity even at high temperatures. Industries such as automotive, aerospace, and construction are increasingly integrating vitrimer-based materials. For instance, vitrimer composites are being utilized in the fabrication of car components, aerospace parts, and heat-resistant construction coatings [8].

A key advantage of vitrimers lies in their recyclability and reusability, aligning with sustainability goals. These materials can be reshaped, repaired, and reused multiple times without degradation in their core properties. This reprocessability not only minimizes waste but also supports the development of a circular economy.

Nonetheless, the widespread adoption of vitrimer technology is currently limited by challenges associated with processing methods and economic feasibility. Achieving commercial success depends on refining production techniques and reducing costs. Despite these hurdles, ongoing research and technological advancements are paving the way for broader application of vitrimers across multiple domains [9].

To unlock the full potential of vitrimers, it is crucial to deepen our understanding of their chemistry, properties, advantages, and limitations. Tackling the issues of manufacturing complexity and cost will be key to maximizing their impact. Thanks to their durability, flexibility, and recyclability, vitrimers hold immense promise in transforming the landscape of polymer materials and driving sustainable innovation in material science [10].

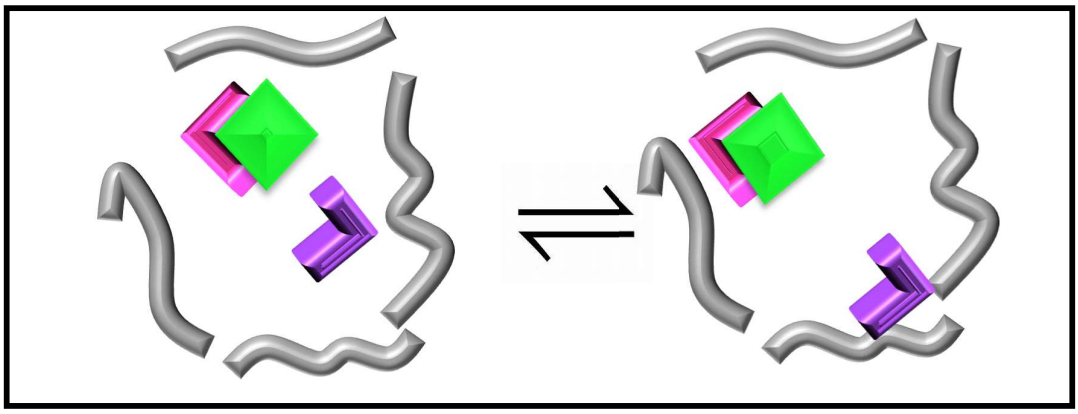


Figure 1.1: Schematic presentation Dynamic covalent Bonds

1.3.1Associative and Dissociative Covalent Adaptable Networks:

Associative Mechanism:

The associative mechanism, also known as "degenerate exchange" or "neighboring group participation", involves the formation of a new bond before the original bond is broken. In other words, the exchange reaction proceeds via a transition state or intermediate in which both the old and new bonds coexist temporarily. This type

of mechanism ensures that the overall connectivity of the polymer network is maintained throughout the reaction process, which is critical for preserving the structural integrity of the material.

In vitrimers, associative mechanisms typically involve bond types such as transesterification, transamination, or exchange reactions involving boronic esters or disulfide bridges. One common example is transesterification, where an ester bond is replaced by another via an alcohol attack. During this reaction, the ester group forms a temporary intermediate with the attacking alcohol, allowing for the rearrangement without breaking down the polymer network [11].

The primary advantage of the associative mechanism is that it allows the material to retain its crosslinked structure even during the exchange process. As a result, the vitrimer behaves like a viscoelastic solid and maintains mechanical strength and dimensional stability while being reshaped or repaired. Moreover, associative exchange reactions are typically reversible and temperature-dependent, allowing for tunable material properties based on the operating conditions [12].

Dissociative Mechanism:

In contrast, the dissociative mechanism involves a two-step process where a covalent bond is first broken, creating a temporary decrease in crosslink density, followed by the formation of a new bond. This means that, at a given moment during the reaction, the polymer network is partially “opened,” allowing for increased chain mobility before reformation occurs.This mechanism is common in systems using reversible covalent chemistries such as Diels-Alder reactions, imine exchange, or urethane bond reversion. For instance, in the Diels-Alder reaction, a cyclic adduct breaks down into a diene and a dienophile at elevated temperatures, increasing molecular mobility. Upon cooling, these components re-form the original bond, restoring the crosslinked structure [13] .

While the dissociative mechanism allows for significant flexibility and reconfigurability, it also comes with potential drawbacks. The temporary loss of network

integrity during the bond dissociation phase can reduce mechanical performance under load or high stress, particularly if the reaction kinetics are slow. Additionally, the reversibility of the dissociative process can lead to changes in the network density over multiple cycles, depending on conditions like temperature or catalyst presence [14].

The choice between associative and dissociative mechanisms greatly influences the behavior of vitrimers. Associative systems offer continuous mechanical strength and long-term durability, making them suitable for structural applications where dimensional stability is crucial. On the other hand, dissociative systems offer more pronounced reshaping and self-healing capabilities, which may be better suited for applications like coatings or adhesives where mechanical load is less critical [15].

In recent developments, researchers have also explored hybrid systems that combine both mechanisms to balance processability with structural performance. Such dual-mechanism systems aim to provide a wider processing window and customizable properties depending on specific application needs [16].

In summary, both associative and dissociative mechanisms are central to the dynamic behavior of vitrimers. Understanding the differences between these pathways enables the rational design of materials with targeted mechanical, thermal, and chemical properties, paving the way for more sustainable and adaptable polymer technologies [17].

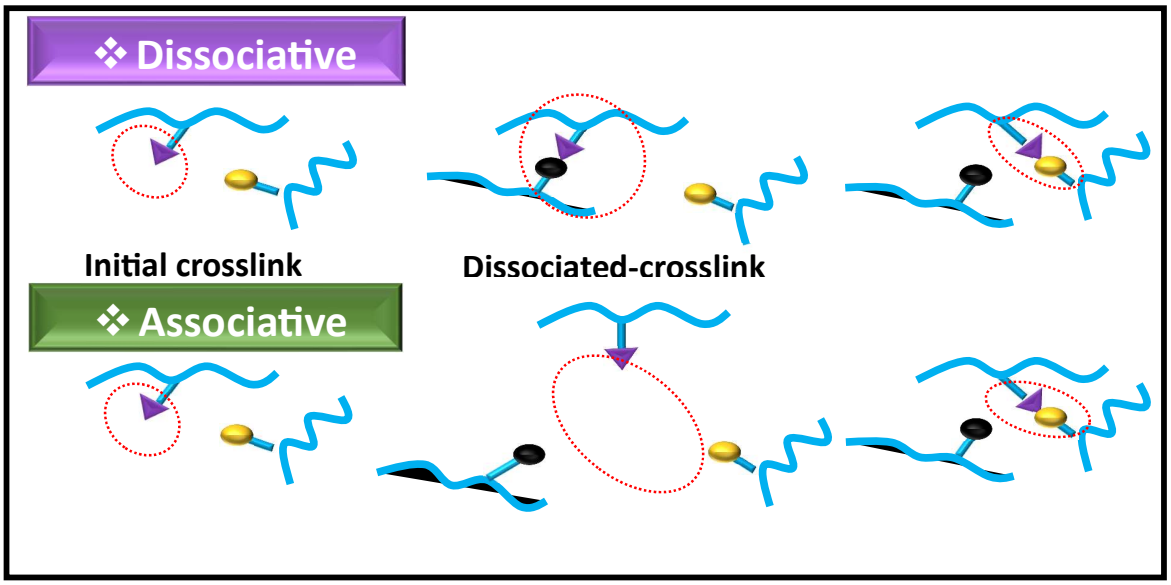


Figure 3: Schematic presentation of Associative and Dissociative Bonds

1.4 Elastomeric Vitrimers

Elastomeric vitrimers are an emerging category of polymeric materials that bridge the gap between conventional elastomers and dynamic covalent networks. They retain the soft, stretchable, and resilient characteristics of traditional elastomers while incorporating the dynamic covalent bond exchange mechanisms that define vitrimer chemistry. These associative exchange reactions enable the polymer network to reorganize without depolymerization, granting the material capabilities such as reprocessability, self-healing, and stress relaxation properties are not typically found in conventional crosslinked elastomers. Unlike thermosets, which are permanently set after curing, elastomeric vitrimers can be reshaped and recycled under appropriate thermal or chemical conditions, making them highly attractive for applications that demand both durability and environmental responsibility. Their ability to maintain mechanical strength while enabling structural rearrangement positions them as innovative materials for a range of advanced uses, including flexible electronics, soft actuators, and recyclable rubber components [18].

1.5 Different types of bonds reaction in Elastomeric Vitrimers

1. Transesterification

Transesterification is a pivotal mechanism in vitrimer chemistry, involving the exchange between ester and hydroxyl groups. This associative exchange maintains the network's crosslink density while allowing for topology rearrangement, imparting properties like reprocessability, self-healing, and recyclability to the material. Catalysts such as zinc acetate or triazabicyclodecene (TBD) are often employed to facilitate this reaction [19].

In elastomeric vitrimers, transesterification enables the material to undergo stress relaxation and network rearrangement at elevated temperatures, facilitating reshaping and repair. For instance, in epoxy-based vitrimers, the presence of β-hydroxy ester linkages allows for transesterification reactions that can be activated thermally, leading to a dynamic network capable of adapting its shape and properties [20].

2. Disulfide Exchange

Disulfide bonds can undergo reversible exchange reactions under thermal or chemical stimuli, making them suitable for dynamic crosslinking in vitrimers. This mechanism imparts self-healing and reprocessing capabilities to the material. However, the exchange reactions can be slower compared to transesterification, and the mechanical properties may be less robust [21].

3. Imine Exchange

Imine bonds, formed through the condensation of amines and aldehydes, can reversibly exchange under ambient conditions. This dynamic covalent chemistry allows for self-healing and recyclability in elastomeric vitrimers. However, imine bonds are sensitive to moisture, which can limit their applicability in certain environments. [22]

4. Dioxaborolane Metathesis

Dioxaborolane metathesis involves the exchange of boronic ester bonds, enabling dynamic crosslinking in vitrimers. This mechanism offers rapid exchange rates and can be activated under mild conditions. However, the sensitivity of boronic esters to moisture and the potential for hydrolysis can pose challenges for long-term stability. [23]

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

The emergence of elastomeric vitrimers marks a significant advancement in the field of sustainable polymeric materials, offering a compelling combination of elasticity, durability, and dynamic covalent adaptability. These materials merge the flexibility of conventional elastomers with the reprocessability and recyclability of vitrimers through dynamic covalent networks—most notably via transesterification reactions. A broad spectrum of crosslinking strategies has been explored to optimize the physical and chemical performance of elastomeric vitrimers, with a growing emphasis on bio-based and catalyst-free systems to support environmental sustainability. This literature survey critically examines recent developments in crosslinking techniques applied to epoxidized natural rubber (ENR-50) and related systems, highlighting innovations such as oxidized starch crosslinkers, imine chemistry, metal-catalyzed transesterification, and polymeric catalysts. These studies not only deepen the understanding of vitrimer behavior under mechanical and thermal stress but also pave the way for designing next-generation elastomers for self-healing, recyclable, and adaptive applications.

1. **Oxidized Starch as a Bio-Based Crosslinker**: Utilizing oxidized starch (OST-57) with ENR-50 forms β-hydroxy ester bonds, resulting in a vitrimer with high elongation at break and elastic recovery. The material exhibits low activation energy for transesterification, enabling efficient reprocessability. [24]
2. **Hydrolyzed Maleic Anhydride with Zinc Acetate Catalyst**: Crosslinking ENR-50 with hydrolyzed maleic anhydride (HMA) in the presence of 1,2-dimethylimidazole (DMI) and zinc acetate dihydrate (ZAD) creates a dynamic network. The ester bonds formed allow for transesterification, providing reprocessability and self-healing capabilities. [25]
3. **Sodium Alginate-Induced Catalyst-Free Crosslinking**: Incorporating sodium alginate into ENR-50 facilitates interfacial dynamic crosslinking through hydroxyl ester bonds without external catalysts. This approach yields a mechanically robust

vitrimer with a segregated structure, enhancing energy dissipation and crack resistance. [26]

4. **Bio-Based Polyols for Enhanced Properties**: Adding glycerol or xylitol to ENR-50 crosslinked with dimer fatty acid (DFA) forms β-hydroxy ester linkages. The choice of polyol influences the network density and mechanical properties, with xylitol increasing modulus and crosslink density, while glycerol provides flexibility. [27]
5. **Dynamic Imine Bonds from Vanillin and Decanediamine**: Creating a fully bio-based vitrimer by reacting ENR-50 with a dynamic crosslinker synthesized from vanillin and 1,10-decanediamine introduces imine bonds. This network offers high tensile strength and elongation at break, along with reprocessability. [28]
6. **Tertiary Amine-Catalyzed Transesterification**: Embedding covalently bonded tertiary amines within epoxy networks catalyzes transesterification reactions. This strategy enhances the dynamic behavior of the vitrimer, allowing for reshaping and recycling. [29]
7. **Phthalic Anhydride and Sebacic Acid as Curing Agents**: Adjusting the ratio of phthalic anhydride to sebacic acid in curing epoxy resins influences the glass transition temperature and mechanical properties. The presence of a transesterification catalyst enables stress relaxation and reprocessing. [30]
8. **Zinc Ionomer as a Polymer Catalyst**: Synthesizing a zinc-containing ionomer, poly(acrylonitrile-co-zinc methacrylate), provides an efficient catalyst for transesterification in epoxy vitrimers. This polymer catalyst enhances mechanical properties and reduces the amount of catalyst required. [31]
9. **Bifunctional Catalysts in Transesterification**: Investigating catalysts like triazabicyclodecene (TBD), zinc acetate, and dibutyltin oxide reveals their efficiency in facilitating transesterification reactions in vitrimers. Computational studies assist in understanding the mechanisms and designing effective catalysts. [32]
10. **Crosslinkers Influencing Electromechanical Properties**: Employing crosslinkers such as P1017, DTPA, and DME with ENR-50 affects the electromechanical behavior of the resulting vitrimers. These crosslinkers enable dynamic exchange mechanisms, impacting stress relaxation and actuation performance. [33]

11. **Dimer Acid and Polyol-Based Vitrimers**: Combining ENR-50 with dimer acid and polyols like glycerol or xylitol forms networks capable of transesterification. The resulting materials exhibit tunable mechanical properties and recyclability. [34]
12. **Imine Bond-Linked Bio-Based Vitrimers**: Utilizing vanillin-derived imine bonds in ENR-50 networks creates fully bio-based vitrimers with dynamic covalent adaptability, offering potential for sustainable applications. [35]
13. **Catalyst-Free Dynamic Crosslinking via Sodium Alginate**: Integrating sodium alginate into ENR-50 matrices enables dynamic crosslinking through hydroxyl ester bonds without external catalysts, enhancing mechanical robustness. [36]
14. **Zinc Acetate-Catalyzed Ester Networks**: Forming ester crosslinks in ENR-50 using hydrolyzed maleic anhydride and catalyzing with zinc acetate dihydrate results in reprocessable networks due to transesterification capabilities [37].
15. **Oxidized Starch-Induced Biodegradable Vitrimers**: Employing oxidized starch as a crosslinker with ENR-50 produces biodegradable vitrimers with dynamic β-hydroxy ester bonds, facilitating environmental sustainability. [38]

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION METHODS

3.1 MATERIALS:

3.1.1 Epoxidized Natural Rubber (ENR):

ENR rubber, Epoxidized Natural Rubber, is a type of synthetic rubber derived from natural rubber. It is produced by chemically modifying natural rubber latex through the introduction of epoxide groups into the polymer chain. Depending on the mol % of epoxide groups there are different types of ENR, **ENR50** which contain 50 mol % epoxide group. This modification enhances its properties, making it suitable for various advanced applications. The increase polarity because of epoxy group and adhesion properties make ENR suitable for adhesives and sealants used in construction, automotive, and industrial applications. It is also used in tire industry. In this study we have used ENR50. [39]

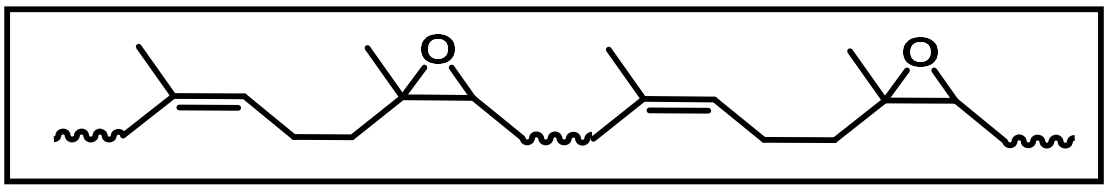


Figure 3.1: Structure of ENR

3.1.2 Pripol-1017

Pripol 1017 is a high-purity dimer acid predominantly composed of dimerized unsaturated fatty acids, produced through the controlled oligomerization of natural vegetable oils. It is valued for its unique combination of flexibility, hydrophobicity, and chemical stability, making it a key raw material in the synthesis of polyamides, polyesters, and epoxy resins. The molecular structure of Pripol 1017, characterized by long hydrocarbon chains and multiple reactive sites, imparts superior resistance to moisture, chemicals, and thermal degradation in the final products. Its widespread use in coatings, adhesives, and lubricants reflects its ability to enhance mechanical properties and extend the lifespan of industrial materials. Additionally, being derived from renewable resources, Pripol 1017 supports sustainable manufacturing practices, aligning with the growing demand for environmentally responsible chemical solutions. [40]

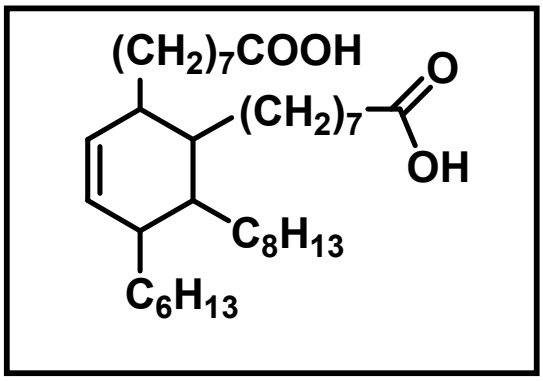


Figure 3.2: Structure of Pripol-1017

3.1.3 1,2- Dimethyl imidazole:

1,2- Dimethylimazole is an organic compound with the chemical formula C5H8N2. It belongs to the class of imidazoles, which are heterocyclic aromatic organic compounds. The molecular weight is 96.13 g. It is appeared as colourless to pale yellow liquid or solid. It is soluble in water and most organic solvents. In chemical research, 1,2-dimethylimidazole is utilized in studying imidazole- based chemistry and developing new materils with specific properties. This compound can serve as an intermediate in the synthesis of various pharmaceutical agents, contributing to the creation of drugs. [41]

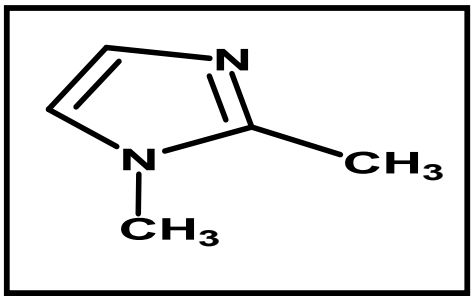


Figure 3.3: Structure of 1,2-Dimethyl Imidazole

3.1.4 Triazabicyclodecene (TBD)

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) is a strong, non-nucleophilic organocatalyst widely employed in polymer chemistry, particularly in the synthesis of vitrimers. Its exceptional basicity and ability to activate ester bonds make it highly effective in promoting transesterification reactions, which are critical for imparting dynamic covalent network behavior to vitrimer systems. In vitrimer formation, TBD facilitates bond exchange under relatively mild conditions, enabling the material to retain its mechanical integrity while allowing for reshaping, self-healing, and recycling. The catalyst's efficiency in driving rapid and reversible transesterification contributes significantly to the vitrimer's adaptability and long-term performance. Moreover, TBD's low toxicity and thermal stability make it a preferred choice for sustainable material design, aligning with the increasing interest in recyclable and reprocessable polymeric materials. [42]

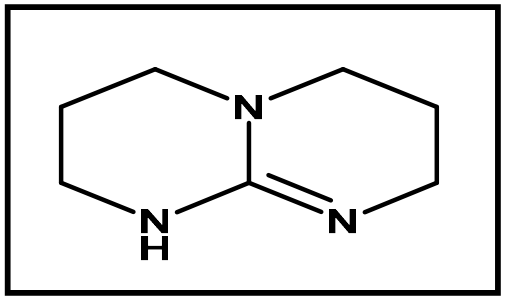


Figure 3.4: Structure of Triazabicyclodecene

3.1.5 Zinc Chloride:

Zinc chloride is an inorganic compound highly soluble in water. The chemical formula is $ZnCl_2$. The combination of hydrochloric acid and $ZnCl_2$, is known as the "Lucas reagent". It is typically seen as white or colorless crystalline solid. It is hygroscopic compound can form various hydrates. Zinc chloride is used as a catalyst or reagent in diverse reactions conducted on an industrial scale. It is a common reagent in the laboratory useful Lewis acid in organic chemistry. [43]

3.2 EXPERIMENTAL

Preparation of sample:

On a two-roll mill ENR-50 rubber is masticated for 2 mins at room temperature with rotor speed of 40 rpm. Then Pripol -1017 is added followed by addition of 1,2 dimethyl imidazole and TBD finally, zinc chloride is added step by step and after that it is compounded for 10 mins. The rubber mixture was then cured in 2 mm sheet by hot compressing molding machine under 10 MPa at 180ºC for 40 mins. [44]

3.3 CHARACTERIZATION

3.3.1 Curing Study

A Moving Die Rheometer (MDR Xgen 100) was used to find out the cure characteristics of composite at 160 ºC - 180 ºC, for 60 min. The uncured sample was placed in a rheometer frequency (1.7 Hz) and then torque generated was measured against the time. The optimum cure time (t_{90}) was obtained from the time-torque curve. Then all the samples were cured as respect their cure time (t_{90}) using a compression moulding machine. The prepared rubber sheets are used for further characterization.

3.3.2 Fourier Transform Infrared Spectroscopy Study

To determine the functional group, FTIR study was performed using an IR-Afnity-1 spectrometer (Shimadzu). Samples were placed directly on the Zinc Selenide (Zn-Se) attenuated total reflectance (ATR) crystal's surface and was analysed in the 4000-400 cm^{-1} frequency range, with a scan rate of 40 and an ATR resolution of 4 cm^{-1}.

3.3.3 Differential Scanning Calorimetry

DSC measurement of sample was carried out with DSC 204 F1 (NETZSCH, Germany) instrument under heating rate of 10ºC per minute and nitrogen flow rate of 40 ml per min. 10-15 mg of material encapsulated in a aluminium pan with pierced lid. The pan was placed into the device at room temperature and heated to 200ºC.

3.3.4 Mechanical Study

A universal testing machine (UTM) (H 10 KT Tinus Olsen) was used to analyse the stress-strain of materials according to ISO 527, with a load cell of 500 N. Dumbbell-

shaped test specimens were utilized and stretched until failure at a cross-head speed of 200 mm min-1 at room temperature. Each sample was tested three times to ensure accuracy, and the mean value was calculated.

3.3.4 Hardness

To study the hardness of rubber composites we used Shore A durometer (BSE testing machine, India). The tests were done as per ASTM D 2240. The test was performed at room temperature. The dimension of test samples was around 6 mm in thickness. An average value of three measurements at different position on the same sample were carried out and reported. [45]

3.3.5 Swelling study

Equilibrium swelling experiments were performed to evaluate the cross-link density of the vitrimer, based on the Flory- Rehner equation. A 2 mm thick square sample of dimensions 10 mm × 10 mm was weighed (m0) and immersed in toluene at ambient temperature for 7 days to achieve equilibrium swelling (m1). Then, the sample was dried in a vacuum oven at 60 ◦C until constant weight. Four specimens were measured for each sample type. density was calculated according to the Flory-Rehner equation. [46]

CHAPTER 4
RESULTS AND DISCUSSIONS

4.1 Result and Discussion

To achieve the esterification reactions between carboxyl groups and epoxy groups, epoxidized natural rubber (ENR) is chosen as matrix. Carboxyl groups of Priopl-1017 were introduced into ENR-50 matrix via ring opening esterification reactions. By utilizing this esterification reactions between carboxyl groups and epoxy groups, the cross-linking is formed. Also zinc chloride is added as a crosslinker. The increased concentration of Priopl-1017 presumably interacts with a greater number of epoxide functionalities, leading to the formation of robust crosslinked network. Composite formulation is present in Table 1.

Table 1: Composition for ENR composites

Sample Code	ENR-50(g)	Pripol-1017 (ml)	Triazabicyclodecene (TBD) (g)	Zinc Chloride (g)	1,2-Dimethyl Imidazole (g)
43-1PR-1.5	50	1.5	0.1	0.6	0.5
43-2PR-1.0	50	1	0.1	0.6	0.5
43-5PR-2.0	50	2	0.1	0.6	0.5
43-6PR-2.5	50	2.5	0.1	0.6	0.5

4.2.1 Rheometric Study

Rheological analysis of the composites are done and presented in the (Figure 4.1 and Table 2). The cure time (t_{90}), which represents the optimal curing time, is determined from the time-torque curve. Subsequently, the rubber samples are subjected to a curing process using a compression moulding machine at a temperature of 180 °C for the optimal duration. The addition of Pripol-1017 and $ZnCl_2$ to the ENR matrix results in an increase in torque value, which indicates the occurrence of crosslinking. The crosslinking process is clearly evident in the elastic torque curves, given in Figure 4.1. At 180 °C, an increase in concentration of Pripol-1017 while maintaining the fixed concentration of zinc chloride, DMI and TBD results in a consistent rise in the maximum torque (M_H) of the ENR-50 composites. Furthermore, it is observed that there is a consistent increase in the minimum torque (M_L) value for ENR composites as shown in **Table 2**. The observed increase in torque suggests the development of a denser crosslinked network, which in turn enhances the mechanical properties. [47]

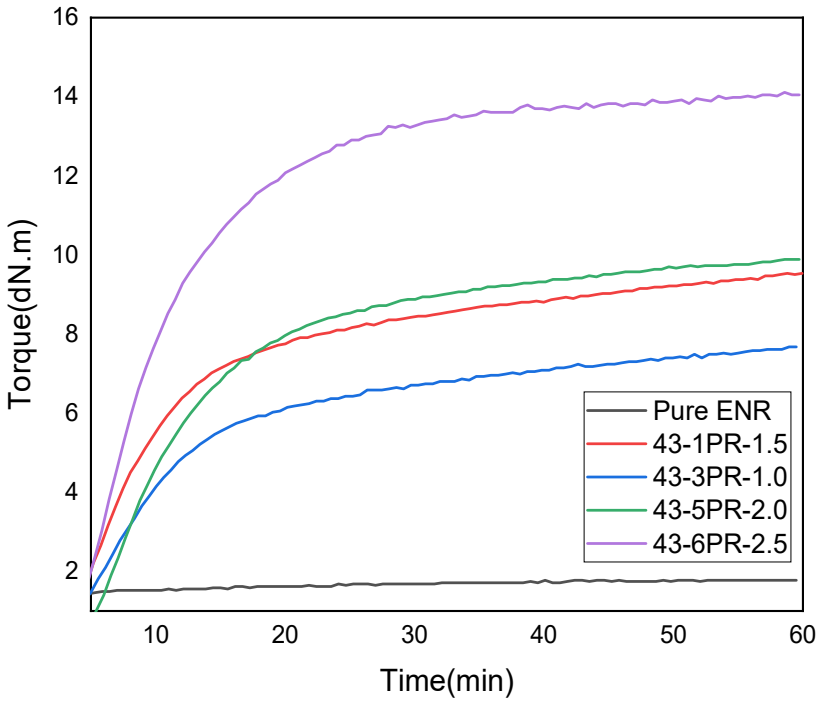


Figure 4.1: Rheometer curves of ENR composites

Table 2: Rheometric Data of ENR composites

Sample Code	Maximum torque(dNm)	Minimum Torque(dNm)	CureTime T_{90}(min)
Pure ENR	1.7897	0.0937	0.04
43-2PR-1.0	7.75	0.4971	37
43-6PR-1.5	9.64	0.2983	33
43-6PR-2.0	9.94	0.2568	28
43-6PR-2.5	14.11	0.1989	23

4.2.2 Fourier Transform Infrared Spectroscopy:

To confirm the formation of the previously mentioned Zn (II) mediated exchangeable crosslinks in ENR matrix, Fourier Transform Infrared Spectroscopy (FTIR) is performed. This technique allows for the identification of newly formed bonds and functionalities in the modified compounds. ENR composite exhibit a C-H stretching frequency at 2960 cm^{-1}. The FTIR spectra of ENR reveal the presence of epoxide groups, as evidenced by peaks appears at 875 and 1251 cm^{-1}. These peaks correspond to the C–O–C stretching vibrations of oxirane rings. Upon addition of Pripol-1017 and 1,2-dimethyl imidazole and TBD, a new peak emerges at a stretching frequency of 1241 cm^{-1}. This peak is attributed to the formation of an ester functional group in ENR matrix and following interaction can be seen in the Scheme 1a. Additionally, presence of some unreacted carboxylic acid groups are detected in the ENR matrix, as indicated by a peak at the stretching frequency of 1704 cm^{-1}. A broad peak is observed in the region of 3250–3600 cm^{-1}, tha appears due to the O–H stretching vibrations, indicating the presence of hydroxyl groups. Interaction between Zn^{2+} and oxygen of oxirane ring is further confirmed by the presence of a peak at 709 cm^{1}. The interactions are represented in Scheme 1b.

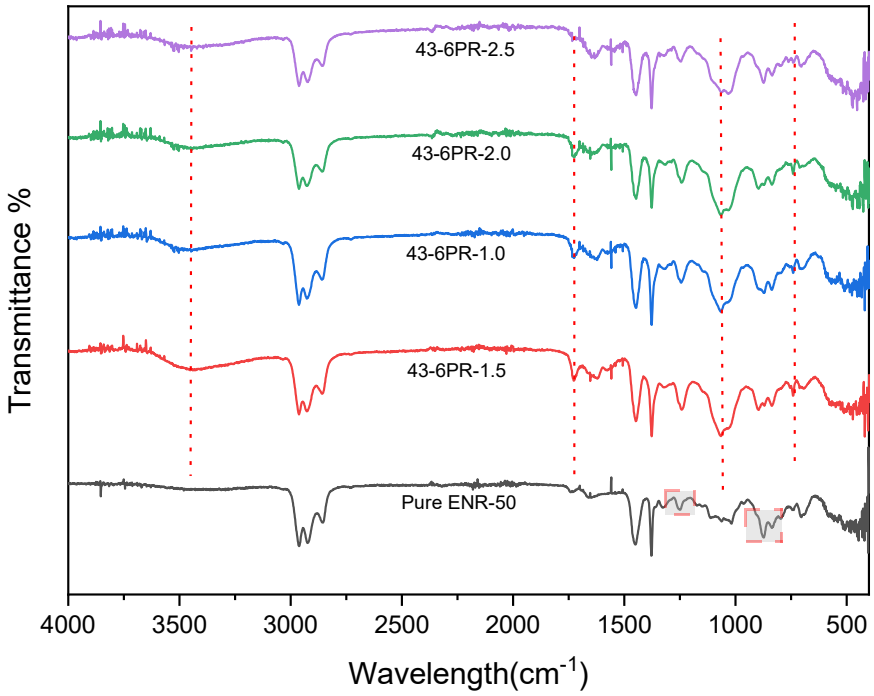
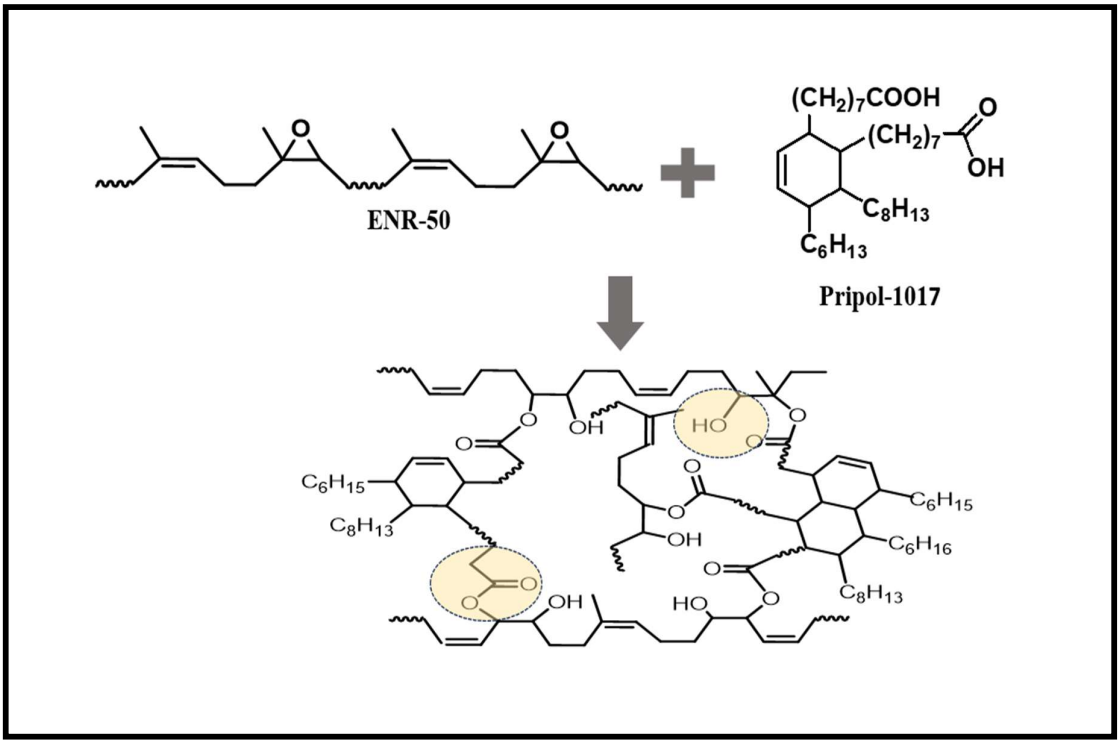
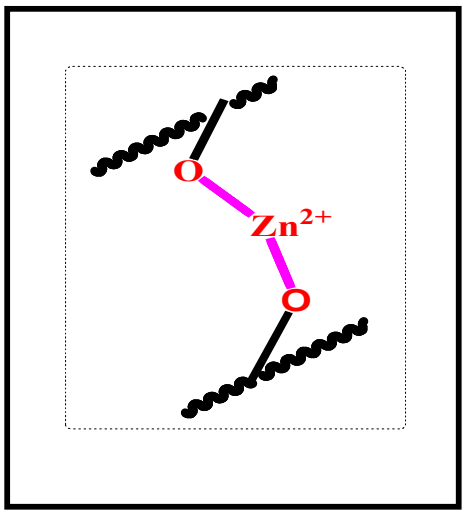


Figure 4.2: FTIR Spectrum for ENR composites



Scheme 1a: Schematic Illustration of ester bond



Scheme 1b: Schematic Illustration of interaction of Zn^{2+} with oxirane ring

4.2.3 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a valuable analytical method that enables the quantification of the glass transition temperatures of materials as a function of temperature. In rubber-based composite, the glass transition temperature (T_g) is directly with chain mobility. The incorporation of crosslinkers, such as Pripol -1017 and $ZnCl_2$, into the ENR rubber matrix results in a reduction in chain mobility within the crosslinked composites. This is due to the formation of additional bonds between polymer chains during crosslinking, which restricts their movement. It is noteworthy that an increase in the concentration of Pripol-1017, is accompanied by a corresponding increase in the glass transition temperature. This is due to the fact that higher concentrations of Pripol-1017 result in an increase in the density of crosslinking, which further restricts the mobility of the polymer chains and thereby raiseing the T_g. The crosslinkers present in the ENR rubber matrix can be adjusted in order to control the material's properties, including its flexibility. This understanding is of great importance for the tailoring the material's performance to specific applications. For example, pure ENR-50 rubber exhibits a T_g of -23 °C. However,

following the addition of Pripol-1017 the T_g shifts to -14.6 ºC for the sample 43-6PR-2.5.

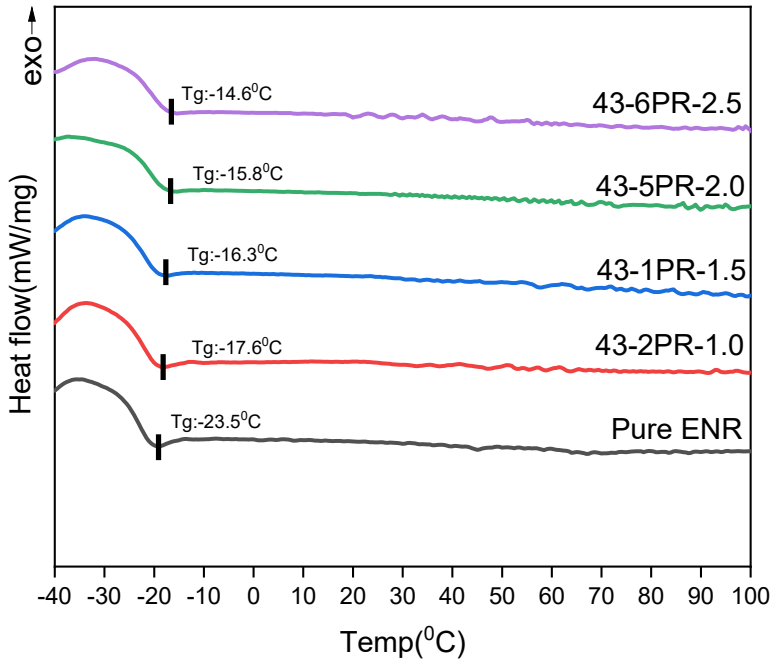


Figure 4.3: DSC curves for ENR composites

4.2.4 Stress- Strain study (UTM)

Stress-strain investigation gives important knowledge on the mechanical performance of ENR composites crosslinked with Pripol-1017. It illustrates that the tensile strength of the composites increases with higher Pripol-1017 content. For the 43-2PR-1.0 sample, the tensile strength is 0.4 MPa, which becomes 0.7 MPa for 43-5PR-1.5 and a maximum of 1.4 MPa for 43-2PR-2.5. This observation highlights the viability of Pripol-1017 in forming dynamic covalent bonds, with subsequent reinforcing the rubber network. In general, a reverse relationship is observed between tensile strength and prolongation at break. This decrease in prolongation is demonstrative of an enhanced stiffness inside the composite, attributable to elevated crosslink density, which in turn restricts molecular mobility and adaptability. Thus, this

study illustrates the tunability of mechanical properties in ENR-50 composites by varying Pripol-1017 substance, providing a pathway for designing materials tailored to specific inustrial needs.

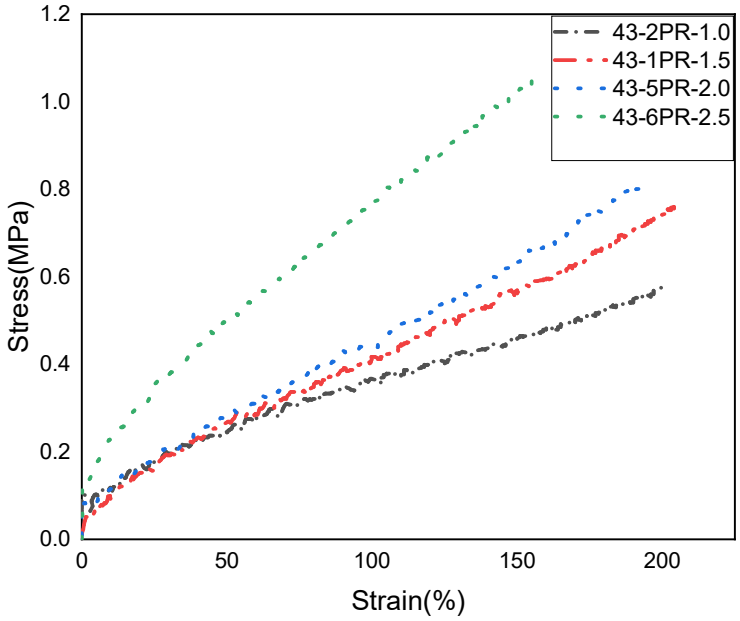


Figure 4.4: Stress-strain curves for ENR composites

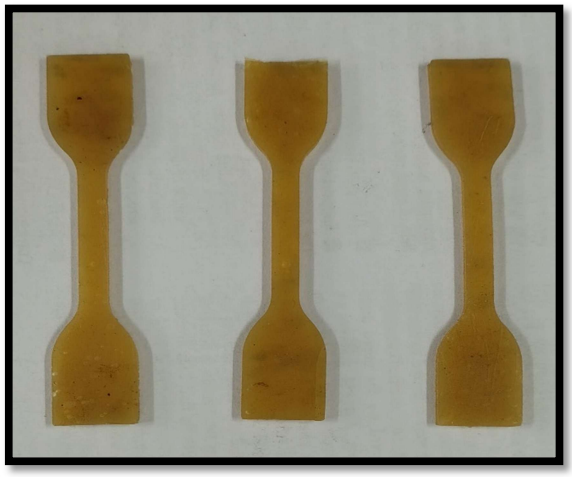


Figure 4.5: Dumb-bell shaped ENR composites

4.4.5 Sweeling Study

Swelling behaviour of the composites is studied in toluene. Hot-pressed pure ENR50 sheets are found to dissolve slowly in toluene, whereas the crosslinked ENR only swells, maintaining its original shape. The crosslinking density of the selected composites is determined from the Flory–Rehner equation. It is found that crosslinking density increases as the concentration of Pripol-1017 as shown in **Table 3**. This also indicates that there is interaction between Pripol-1017 and the epoxide group of ENR rubber contributing to the crosslinking in ENR composite.

Table 3: Swelling Data for ENR composites

Sample code	Intial weight(g)	Swell weight (g)	Crosslinking density (mol cm^{-3})
43-2PR-1.0	0.3931	2.20	3.78
43-2PR-1.5	0.4054	2.30	4.01
43-2PR-2	0.4378	2.43	4.95
43-2PR-2.5	0.4158	2.54	5.53

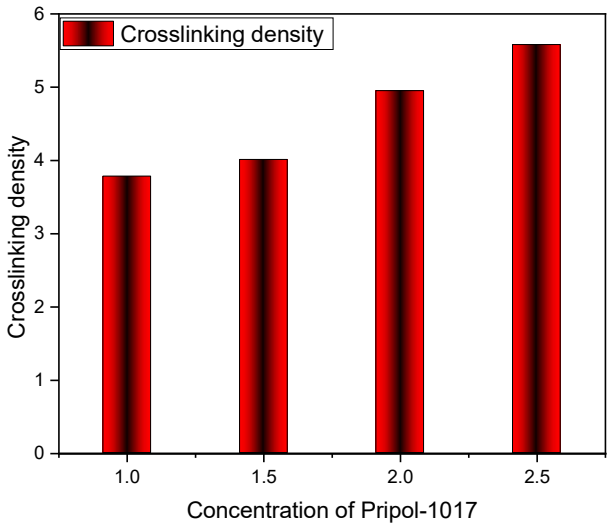


Figure 4.6: Swelling for ENR composites

4.4.5 Hardness

A durometer is an instrument used to measure the hardness of materials, especially polymers, elastomers, and rubbers. It works by assessing the depth of indentation made by an indenter under a standard load—harder materials show less indentation and thus yield higher durometer readings.

In this work, increasing the concentration of Pripol-1017 enhances the interaction between the epoxy groups of ENR-50 and the carboxylic (-COOH) groups of Pripol-1017. This increases interaction promotes the formation of a greater number of crosslinks within the material. The highest hardness is shown by 43-2PR-2.5 which is in accordance with the results found for this composite in earlier studies.

Table 4: Hardness for ENR composites

Sample Code	ENR-50(g)	Pripol-1017(ml)	Durometer Hardness (Shore A)
43-2PR-1.0	50	1.0	45
43-2PR-1.5	50	1.5	50
43-2PR-2.0	50	2.0	55
43-2PR-2.5	50	2.5	60

CHAPTER 5

SUMMARY, CONCLUSION AND FUTURE SCOPE

5.1 Summary

This research focused on the development of crosslinked elastomers through dynamic covalent interactions to transform Epoxidized Natural Rubber (ENR) into vitrimeric materials. A novel formulation comprising Pripol-1017, 1,2-Dimethylimidazole, and $ZnCl_2$ is employed to induce dynamic crosslinking in ENR-50. We have systematically varied the content of Pripol-1017 in the formulation to optimize the crosslink density and mechanical performance of the resulting elastomers. Comprehensive characterization techniques, including Fourier Transform Infrared Spectroscopy, rheometry, and swelling studies, confirmed the successful formation of dynamic crosslinks. An increase in the glass transition temperature as studied by DSC, with higher Pripol-1017 content further validated the crosslinking process. Among the tested formulations, the sample designated as 43-2PR-2.5 exhibites notable mechanical performance, achieving a tensile strength of 1.1 MPa.

5.2 Conclusion:

We have successfully synthesised crosslinked elastomers utilising dynamic interactions, representing a significant advancement in the field. The principal objective of our research was to transform Epoxidized Natural Rubber (ENR) into vitrimers by employing a distinctive blend of Pripol-1017, 1,2-Dimethylimidazole, and $ZnCl_2$. Experiments was conducted using varying quantities of Pripol-1017 to form crosslinks in ENR rubber, with the objective of optimizing the process. The crosslinking process is found to be influenced by Pripol-1017. The comprehensive investigation that involved rheometry and swelling study, confirms the presence of crosslinks this study is also supported from DSC study. These findings demonstrate a significant advancement in ENR-based vitrimer technology and contribute valuable insights into the design of high-performance vitrimers.

5.3 Future Scope

Elastomeric vitrimers are a promising materials in the broader domain of materials science. They possess the ability to withstand high temperatures like thermosets, while also being able to be reprocessed like glass. This unique features make them a potential contender for recyclable thermoset composites. Elastomeric vitrimers could possess a diverse array of uses in the future, including many obstacles and opportunities.

1. The issue of recyclability holds significant relevance. A key benefit of vitrimer materials is their capacity for being recycled. Thermoset materials have historically shown little potential to be recycled because they generate permanent chemical connections during the curing process. On the other hand, vitrimer materials can be recycled at elevated temperatures, providing a more environmentally friendly option.

2.Research on the mechanical characteristics of vitrimer composites is of paramount importance. Another aspect of interest involves comparing the mechanical characteristics of elastic vitrimers and commercially available elastomers. Comprehending these characteristics will aid in the creation of vitrimers that have the potential to equal or surpass the performance of current materials

3.Elastomeric vitrimers have a promising future, offering abundant prospects for research and development. The possibility of merging the benefits of thermosets and thermoplastics into one substance has the potential to lead to substantial progress in the field of materials science.

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